

# A model for the formation energies of alanates and boranates

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We develop a simple model for the formation energies (FEs) of alkali and alkaline earth alanates and boranates, based upon ionic bonding between metal cations and  $\text{AlH}_4^-$  or  $\text{BH}_4^-$  anions. The FEs agree well with values obtained from first principles calculations and with experimental FEs. The model shows that details of the crystal structure are relatively unimportant. The small size of the  $\text{BH}_4^-$  anion causes a strong bonding in the crystal, which makes boranates more stable than alanates. Smaller alkali or alkaline earth cations do not give an increased FE. They involve a larger ionization potential that compensates for the increased crystal bonding.

The large scale utilization of hydrogen as a fuel crucially depends on the development of compact storage materials with a high mass content of hydrogen.<sup>1</sup> Over the last decade alanates and boranates have been studied extensively because of their potential use as hydrogen storage materials.<sup>1,2</sup> These materials consist of a lattice of metal cations and  $\text{AlH}_4^-$  or  $\text{BH}_4^-$  anions, respectively. The ideal hydrogen storage material should have a high gravimetric hydrogen density, which requires the use of light metals. Moreover, the formation energy (FE) of such a material has to be such that it is stable at room temperature, yet it has to decompose at low temperature to release its hydrogen. In principle a large variety of alanates and boranates can be synthesized by changing the metal cations, which can be used to tune the formation energy.<sup>3</sup>

Since synthesis is a very time consuming effort, there is a need for a materials specific theory with a predictive power for the FE. At present the state of the art is formed by first principles calculations based upon density functional theory (DFT). Several papers have been dedicated to trends in the DFT FEs of alanates and boranates.<sup>3,4,5,6,7</sup> There exists a surprising variety of crystal structures among these compounds. In DFT calculations the crystal structure with the lowest energy has to be searched for each compound, and the cell parameters and the atomic positions have to be optimized. This procedure also makes DFT calculations a very time consuming effort. A simple theory would help to understand the trend in the FEs of alanates and boranates.

Our aim is to construct a simple model for the FEs at 0 K of alkali alanates and boranates ( $\text{MAH}_4$ ,  $M = \text{Li, Na, K}$ ;  $A = \text{Al, B}$ ) and of their alkaline earth counterparts ( $M'(\text{AH}_4)_2$ ,  $M = \text{Mg, Ca}$ ), avoiding the use of the actual crystal structure. We assume that these compounds can be described by ionic bonding between  $M^+$  or  $M'^{2+}$  cations and  $\text{AH}_4^-$  anions. Our model for the FE,  $\Delta E_f$ , is based upon a Born-Haber cycle,<sup>8</sup>

$$\Delta E_f = E_{\text{elem}} + E_{\text{ions}} + E_{\text{crys}}. \quad (1)$$

Starting from bulk elemental solids and  $\text{H}_2$  molecules,  $E_{\text{elem}}$  is the energy required to atomize the solids and the molecules. The  $E_{\text{elem}}$  of the bulk solids are listed in Table I. We use a value of 4.48 eV for the dissociation energy of  $\text{H}_2$ .<sup>9</sup>

The second step is to create  $M^+$ ,  $M'^{2+}$  and  $\text{AH}_4^-$  ions from the atoms, represented by the energy  $E_{\text{ions}}$ . The contribution to  $E_{\text{ions}}$  from the  $M^+$  ions is simply the first ionization potential (IP) and from the  $M'^{2+}$  ions it is the sum of the first and second IPs. The numbers  $\Sigma IP$  are given in Table I. We calculate the contribution to  $E_{\text{ions}}$  from the  $\text{AH}_4^-$  anions as follows. First an electron is added to an Al or B atom, which lowers the energy by the atomic electron affinity (EA). These atoms then have four valence electrons that are used to form covalent bonds with four hydrogen atoms. Using EAs of 0.44 eV and 0.28 eV for Al and B, and 2.91 eV and 3.45 eV for the Al-H and B-H bond strengths,<sup>9</sup> we calculate FEs of  $-12.08$  eV and  $-14.08$  eV for the  $\text{AlH}_4^-$  and  $\text{BH}_4^-$  anions.

The final step consists of constructing the crystal from the  $M^+$  (or  $M'^{2+}$ ) and  $\text{AH}_4^-$  ions, which is represented by the energy  $E_{\text{crys}}$ . We use a simple Born model for the potential between cations and anions. It consists of an attractive Coulomb potential between point charges at the centers of the ions plus a repulsive short-range potential  $\propto r^{-\bar{n}}$ , where  $\bar{n}$  is the average Born exponent.  $E_{\text{crys}}$  is then given by<sup>10</sup>

$$E_{\text{crys}} = \frac{M_c Z_A Z_C e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{\bar{n}}\right), \quad (2)$$

where  $Z_A = -1$  and  $Z_C = +1, +2$  are the valencies of the anions and the cations, respectively, and  $r_0$  is the shortest cation-anion distance in the lattice.  $M_c$  represents the Madelung constant, which depends upon the type of lattice.<sup>10</sup>

Note that in all compounds considered here the  $\text{AlH}_4^-$  and  $\text{BH}_4^-$  anions have a tetrahedral geometry. However, in the Born model of Eq. (2), we have approximated these tetrahedra by spheres. Our motivation for this is that we

TABLE I: Ionic radii,  $R_{\text{ion}}$  (Å), summed ionization potentials,  $\Sigma IP$  (eV), dissociation energies for the elemental bulks,  $E_{\text{dis}}$  (eV), and the Born exponents,  $n$ . Values are taken from Refs. 9 and 11

	Li	Na	K	Mg	Ca	B	Al
$R_{\text{ion}}$	0.90	1.16	1.52	0.86	1.14		
$\Sigma IP$	5.39	5.14	4.34	22.67	17.98		
$E_{\text{dis}}$	1.64	1.08	0.93	1.48	1.81	5.81	3.38
$n$	5	7	9	7	9	7	9

are interested in a simple model of  $E_{\text{crys}}$  without having to take into account the full details of the crystal structure. The cation-anion distance then is the sum of the ionic radii of the cation and the anion,  $r_0 = r_C + r_A$ . Since the cations we consider are mostly octahedrally coordinated, we use standard ionic radii  $r_C$  of 6-fold coordinated alkaline and alkaline earth ions, see Table I.<sup>11</sup> As the radius of the anions  $r_A$  we use the Al-H and B-H bond lengths, which are 1.62 Å and 1.20 Å, respectively.  $r_A$  then roughly corresponds to the average of the maximum radius of an  $\text{AH}_4^-$  ion ( $A = \text{Al}, \text{B}$ ) and the minimum radius, which is the radius of the central atom A. The values obtained for the cation-anion distance  $r_0$  then correspond to the average of the cation-Al/B and cation-H distances in the crystal.

Avoiding the full details of the crystal structure also leads to using average values for the Madelung constants  $M_c$  in Eq. (2). The alkali aluminates and borates have an AB type lattice, where A is the alkali cation, and B is the borate or aluminate anion. The variation of the Madelung constant over different AB lattices is relatively small, so we use an average value  $M_c = 1.76$ . The root mean square deviation (rms) averaged over all AB lattice types is 4%. A similar reasoning holds for the alkaline earth aluminates and borates. They have an  $\text{AB}_2$  lattice, whose average Madelung constant is  $M_c = 2.40$  with a rms deviation of 4%.

Fig. 1 shows the most important results, i.e. the FE calculated with the model represented by Eqs. (1) and (2), compared to experimental values.<sup>12</sup> For some of the materials the experimental FE is not known. Therefore we have also performed first principles DFT calculations. We use the projector augmented wave (PAW) method,<sup>13,15</sup> and the PW91 generalized gradient approximation (GGA),<sup>14</sup> as implemented in the Vienna *ab initio* simulation package (VASP).<sup>16,17,18,19</sup> To integrate the Brillouin zone we apply the tetrahedron scheme. The  $\mathbf{k}$ -point mesh and the plane wave kinetic energy cutoff (700 eV) are chosen such, that total energies are converged to a numerical accuracy of 1 meV per formula unit.<sup>20</sup> The structures of  $\text{LiAlH}_4$ ,<sup>21</sup>  $\text{NaAlH}_4$ ,<sup>21</sup>  $\text{Mg}(\text{AlH}_4)_2$ ,<sup>21</sup>  $\text{Ca}(\text{AlH}_4)_2$ ,<sup>22</sup>  $\text{Ca}(\text{BH}_4)_2$ ,<sup>23</sup>  $\text{KAlH}_4$ ,<sup>24</sup> and of the alkali borates<sup>7</sup> are taken from the literature. We additionally relaxed the atomic positions, but the relaxations were small and had only a minor effect on the total energies. Our calculated values compare well to those obtained in

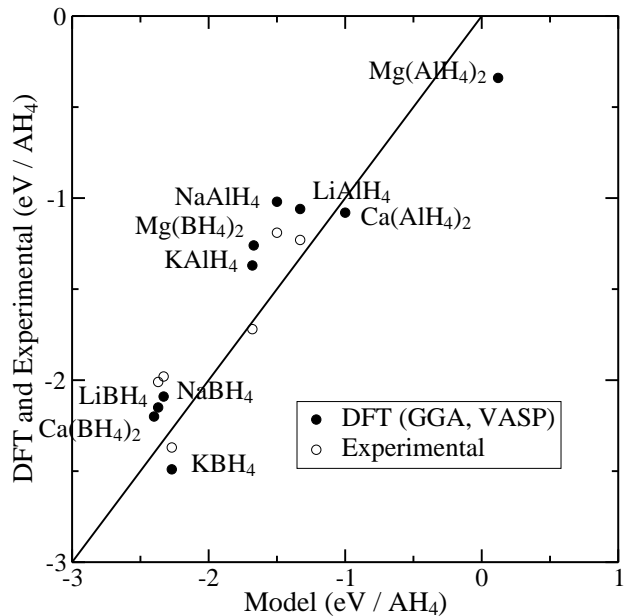


FIG. 1: Model formation energies (eV/AH<sub>4</sub>) compared to DFT and experimental values.<sup>12</sup>

previous calculations.<sup>3,4,6,7,25</sup> Details on  $\text{Mg}(\text{BH}_4)_2$  will be published elsewhere.<sup>26</sup>

Fig. 1 shows that, despite its simplicity, the model gives FEs that are in quantitative agreement with both the experimental, and the calculated DFT values. The rms deviation of the model with the experimental and the DFT values is 0.27 and 0.33 eV/AH<sub>4</sub>, respectively. Note that these numbers are comparable to the rms deviation between the experimental and the first principles values, 0.19 eV/AH<sub>4</sub>, which represents the state-of-the-art. An obvious source of error is our neglect of the details of the crystal structure, e.g., by using an average Madelung constant in Eq. (2). Changing the Madelung constant by 5% changes the FE of the alkali compounds by 0.4 eV/AH<sub>4</sub> and that of the alkaline earth compounds by 0.7 eV/AH<sub>4</sub>. As these numbers are larger than the rms deviation of the model, one can conclude that the details of the crystal structure are relatively unimportant.

The model also seems to work reasonably well for some other borates. The model FE for  $\text{Sc}(\text{BH}_4)_3$  is 0.37 eV/BH<sub>4</sub> higher than the DFT value calculated by Nakamori *et al.*,<sup>3</sup> which is within the rms error bar given above. The model FE for  $\text{Zn}(\text{BH}_4)_2$  and  $\text{CuBH}_4$  are 0.6 and 0.8 eV/BH<sub>4</sub> higher than the DFT values, respectively. For cations with a nominal charge  $Z_C = 4$ , such as Zr or Hf, the model breaks down. The model FE then deviates by 2.5 eV/BH<sub>4</sub> from the DFT values.<sup>3</sup> As can be seen from Eq. (2), for large  $Z_C$   $E_{\text{crys}}$  becomes sensitive to small changes in the Madelung constant and the ionic radius of the cation, or in other words, to the details of the crystal structure.

Fig. 1 shows that borates are generally more stable

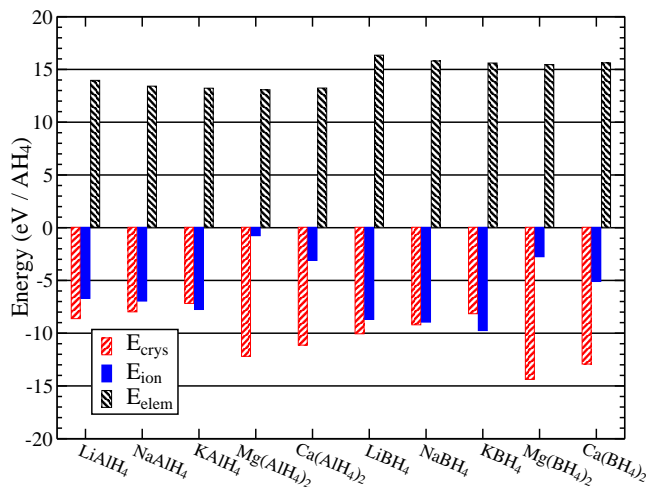


FIG. 2: The contributions to the formation energy (eV/AH<sub>4</sub>) according to Eq. (1).

than aluminates. The origin of this stability can be analyzed by decomposing the FE into the contributions according to Eq. (1), which is shown Fig. 2. The differences in formation energy of the elements  $E_{\text{elem}}$  are to a large degree compensated by the differences in the formation energies  $E_{\text{ions}}$  of the ions from the atoms. The ionic crystal energy  $E_{\text{crys}}$  of the borates is however significantly larger than that of the aluminates, which results in a larger stability of the latter. This is a size effect since the BH<sub>4</sub><sup>-</sup> anions are significantly smaller than the AlH<sub>4</sub><sup>-</sup> anions.

It has been observed that the dissociation energies of

complex alkali hydrides into simple alkali hydrides increase with the atomic number of the alkali atom.<sup>27</sup> For the FEs from the elements the overall trend is not that clear.  $E_{\text{elem}}$  and  $E_{\text{ions}}$  both decrease with increasing atomic number, see Fig. 2, which increases the stability. However, this is almost compensated by  $E_{\text{crys}}$ , which increases with the cation radius  $r_C$ .

In the alkaline earth series the FE decreases with the atomic number. The dominant effect is a decreasing  $E_{\text{ions}}$ , which is due to a decrease in the ionization potentials of the cations, see Table I.

To summarize we constructed a model for the formation energies (FEs) of alkali and alkaline earth aluminates and borates from the elemental solids and H<sub>2</sub> molecules. The model is based upon ionic bonding between metal cations and AlH<sub>4</sub><sup>-</sup> or BH<sub>4</sub><sup>-</sup> anions. It can be constructed using simple energy values that are available in the literature and it does not make use of explicit crystal structure information. Compared to experimental values, the model FEs have a similar accuracy as calculated DFT values. The trends in the FEs over the series of compounds can be analyzed in terms of the individual contributions to the model.

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